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DECLARATION

I, Manfred Groner, Dr. sc. nat. ETH, European Patent Attorney, working with Isler & Pedrazzini AG, do hereby solemnly and sincerely declare:

THAT I am conversant with the German and English languages; and

THAT to the best of my knowledge and belief the attached document is a true and correct translation from German into English of Swiss patent application No. 0149/03 in the name of Eidgenössische Technische Hochschule Zürich.

Signed this 23th day of December 2009

Dr. Manfred Groner

Method for production of a B/N/C/Si ceramic from a
borazine precursor, ceramics made by said method and
use of the ceramic made by said method

5 The production of ceramics and, in particular, high-performance ceramics from borazine precursors is known. Nitride and carbonitride ceramics containing boron and silicon are of particular importance because of, in particular, their high thermal stability and oxidation
10 resistance.

High-temperature-stable silicon borocarbonitride ceramics from silylalkylborazines and processes for producing them have become known from WO 02/22625. The
15 borazines used as precursor each have the structural element Si-C-B-N. To produce a silicon borocarbonitride ceramic, a silylalkylborane is pyrolyzed in an inert or ammonia-containing atmosphere at temperatures of from -200°C to +2000°C. The resulting product is calcined in
20 an inert or ammonia-containing atmosphere at temperatures of from 800°C to 2000°C. N-Si-C-B-N structural units are said to be present in such a ceramic.

25 New molecular and polymeric precursors for B/N/C/Si ceramics are known from the thesis ETH No. 14179 by Anja Krummland. These ceramics are produced using B-triethynylborazine as starting material. Borazines as precursor are prepared by catalytic hydrosilylation. In
30 particular, B-tris(trichlorosilylvinyl)borazine is crosslinked via hydrolyzable SiCl₃ and Si(OR)₃ groups by means of a sol-gel process and by means of an ammonolysis. The resulting ceramics are said to be hard, amorphous and homogeneous and stable up to at
35 least 1500°C. However, these ceramics generally contain by-products which are difficult to remove. The production of a pure ceramic is thus comparatively

complicated. NH_4Cl , for example and in particular, occurs as by-product.

It is an object of the invention to provide a process
5 of the type mentioned which avoids the abovementioned disadvantages. The process should nevertheless make it possible to achieve a comparably high yield.

The process is achieved by the borazine precursor being
10 B-tris(hydrosilylvinyl)borazine (also referred to as B-tris(silylvinyl)borazine) and this being converted into ceramic by pyrolysis. It has surprisingly been found that the ceramic produced by this process is essentially pore-free and displays only minimal
15 shrinkage in the conversion into a high-temperature ceramic. The borazine precursor used is liquid at room temperature and can thus be processed particularly readily. For example, this borazine precursor can be applied by painting with a brush or by spraying.

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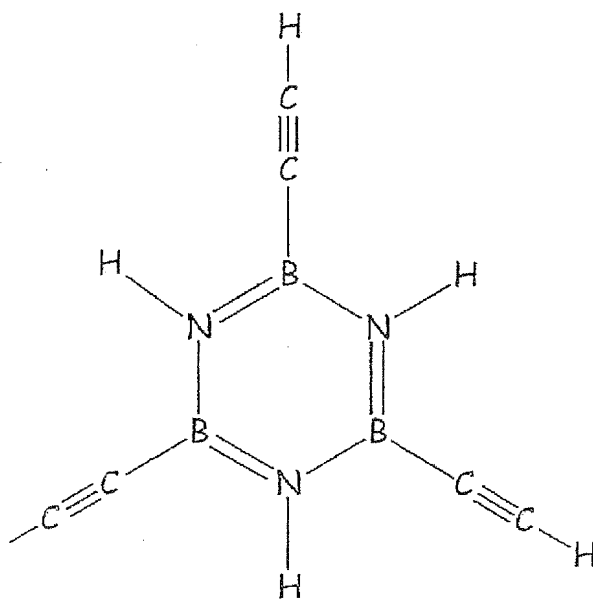
The purity of the ceramic obtained is surprisingly high and the pyrolysis produces, apart from hydrogen, essentially no further gaseous products which are given off. In addition, the yield is exceptionally high. An
25 important advantage of the process of the invention is that no crosslinking and polymer formation is necessary. The borazine precursor can be converted directly into ceramic by means of the pyrolysis. Conversion into a high-temperature ceramic is readily
30 possible by means of a treatment at higher temperature.

In addition, it has unexpectedly been found that the ceramic produced by this process has semiconducting properties. The high conductivity results from the
35 presence of double bonds and the substantial absence of oxygen. The ceramic of the invention is suitable, in

particular, for the production of heating elements which can, inter alia, be operated without contacts and are particularly air-stable. A further advantageous application is an antistatic coating, for example for the inside of pipes. Static charging can be avoided by means of such a coating. In addition, the coating is comparatively very stable both thermally and chemically.

10 The invention is illustrated below with the aid of examples.

The starting point of the synthesis is triethynylborazine of the formula I.



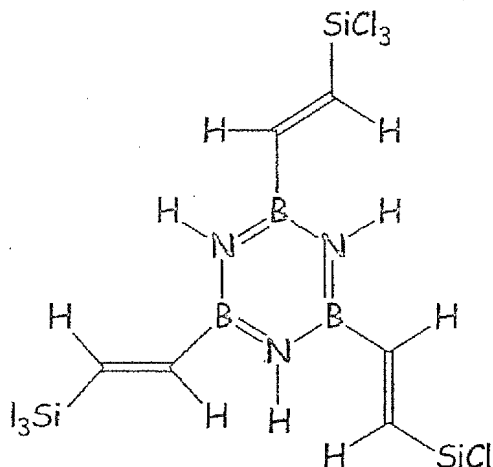
I

15

The synthesis of this compound is known and is disclosed, for example, in EP 0570247 A1. B-Tris(trans-trichlorosilylvinyl)borazine can be prepared from this compound.

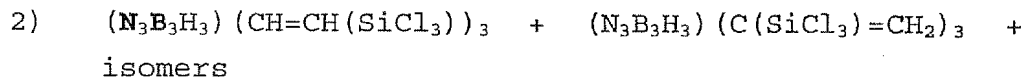
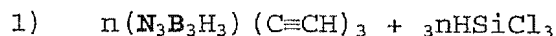
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Preparation of B-tris(trans-trichlorosilylvinyl)borazine (formula II)



5

Reaction equations:



10

Triethynylborazine	10 g,	65.6 mmol
Trichlorosilane	54.2 g,	400 mmol
Platinum on carbon (1%)	1 g,	0.05 mmol of Pt

15 10 g of triethynylborazine are dissolved in 300 ml of toluene, and 1 g of Pt/C(1%Pt) is added. The trichlorosilane is then added via a dropping funnel and the mixture is stirred vigorously, so that the reaction commences. At a reaction temperature of about 80°C for
20 12 hours, the components react completely. The Pt/C is subsequently filtered off and excess trichlorosilane and the toluene are then distilled off. The reaction product is finally dried in a high vacuum and is obtained in quantitative yield. The prepara-
25 tion/isolation of the compound (B-tris(trans-trichloro-

silylvinyl)borazine in pure form is effected by fractional crystallization of the reaction product from hexane at -30°C . The various isomers can be distinguished quite simply by means of NMR spectra.

5

^1H -NMR (C_6D_6): 6.85/6.22 (3J = 21.3); 4.60

^{11}B -NMR: 34.0

^{13}C -NMR: 137.4/154 (b)

^{29}Si -NMR: -3.3

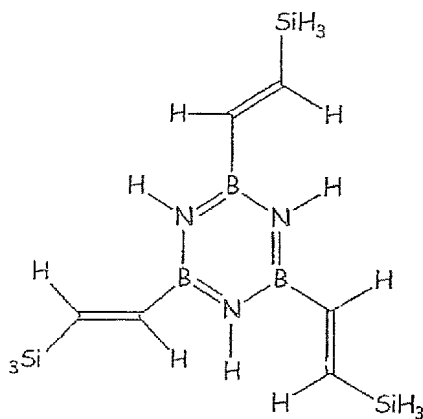
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In addition, the identity of this compound has been confirmed by single-crystal structure analysis.

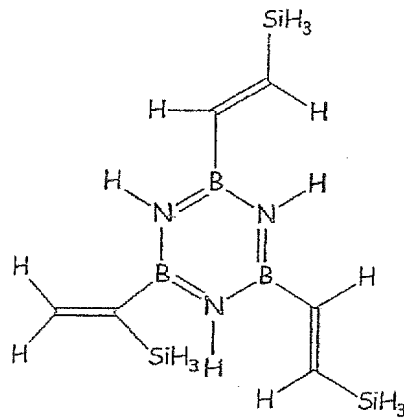
Preparation of B-tris(hydrosilylvinyl)borazine (formula II or IIIa to IIIc)

15

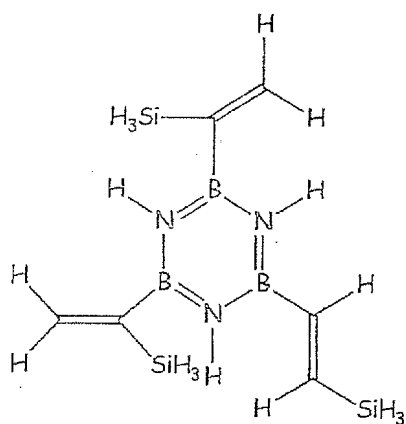
Example 1:



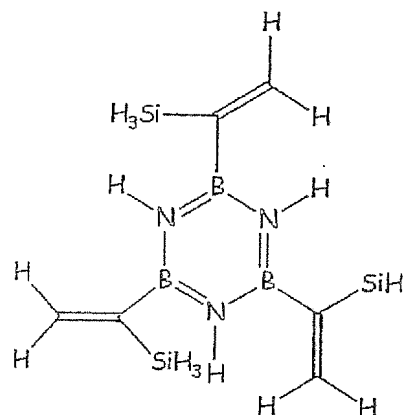
III



IIIa



IIIb



IIIc

Reaction equations:

- 5 1) $4(\text{N}_3\text{B}_3\text{H}_3)(\text{CH}=\text{CH}(\text{SiH}_3))_3 + 9 \text{ AlH}_4$
 2) $4(\text{N}_3\text{B}_3\text{H}_3)(\text{CH}=\text{CH}(\text{SiH}_3))_3 + \text{isomers} + \text{LiCl} + 9 \text{ AlCl}_3$
 B-tris(trans-trichlorosilylvinyl)borazine
 10 g, 17.9 mmol
 LiAlH₄ 1.6 g, 42.1 mmol

10

1.6 g of LiAlH_4 are suspended in 10 ml of THF and cooled to -20°C . 10 g of B-tris(trans-trichlorosilylvinyl)borazine dissolved in 80 ml of THF are then added dropwise over a period of about 1 hour while maintaining the temperature. After the reaction mixture has warmed to room temperature, it is stirred for another 12 hours. 20 ml of hexane are then added in order to precipitate excess LiAlH_4 and part of the $\text{AlCl}_3/\text{LiCl}$. The solid is filtered off and washed with 10 ml of hexane. The filtrate is freed of the solvents and taken up in a mixture of 150 ml of hexane and 50 ml of toluene. The by-product LiCl is once again filtered off from this suspension. The solvents are removed from

the filtrate to give a colorless, highly viscous liquid which becomes solid after drying in a high vacuum. The isomers IIIa to IIIc can be prepared correspondingly.

5 $^1\text{H-NMR}$ (C_6D_6): 4.26/4.96/6.38/6.75 ($3J_{\text{vinyl-trans}} = 21.6 \text{ Hz}$; $3J_{\text{Hsi-CH}} = 2.8 \text{ Hz}$)

 $^{11}\text{B-NMR: } 33.4$ $^{13}\text{C-NMR: } 135/153.7 \text{ (b)}$
$$^{29}\text{Si-NMR: } -63.1 \text{ (J}_{\text{Si-H}} = 199 \text{ Hz)}$$

10

Preparation of B-tris(hydrosilylvinyl)borazine

Example 2:

15 Reaction equations:

$$1) \quad (\text{N}_3\text{B}_3\text{H}_3) (\text{CH}=\text{CH}(\text{SiCl}_3))_3 + 9 \text{LiHB}(\text{Et})_3$$
$$2) \quad (\text{N}_3\text{B}_3\text{H}_3) (\text{CH}=\text{CH}(\text{SiH}_3))_3 + \text{isomers} + 9 \text{ LiCl} + 9 \text{ B}(\text{Et})_3$$

B-tris(trans-trichlorosilylvinyl)borazine

20

10 g, 17.9 mmol

LiHB(Et)₃ 1M in THF 161.1 ml, 161.1 mmol of
LiHB(Et)₃

10 g of B-tris(trans-trichlorosilylvinyl)borazine are dissolved in 200 ml of THF and cooled to -50°C. 161.1 ml of a 1 molar solution of LiHB(Et)₃ in RHF are added thereto. After the reaction mixture has warmed to room temperature, it is stirred for another 12 hours to complete the reaction. The reaction solution is then evaporated to a volume of about 30 ml, which results in white LiCl starting to precipitate. To precipitate all of the LiCl, 100 ml of toluene are added. The solid is filtered off and washed with 10 ml of toluene. The solvents and the by-product triethylborane are distilled off from the filtrate under reduced pressure. The isomers can also be prepared in this way.

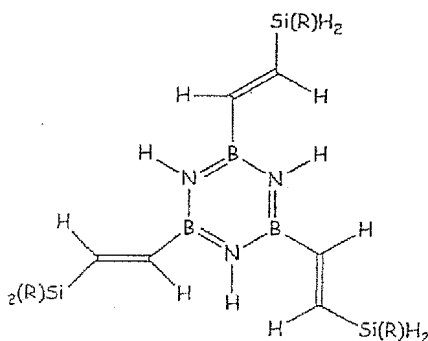
Further suitable precursors which can be converted directly into ceramic by pyrolysis are the compounds of the formulae IVa-IVb and V to Vd, where R is a hydrogen, alkyl, in particular methyl, a phenyl or amine. The abovementioned synthetic methods are applicable to these compounds, for the methyl or phenyl compounds in each case using PhSi(H)Cl_2 or $\text{CH}_3\text{Si(H)Cl}_2$, $\text{Ph}_2\text{Si(H)Cl}$ or $(\text{CH}_3)_2\text{Si(H)Cl}$. The subsequent hydrogenation can likewise be carried out as mentioned above.

The analytical data for B-tris((phenyldihydrosilyl)-vinyl)borazine are:

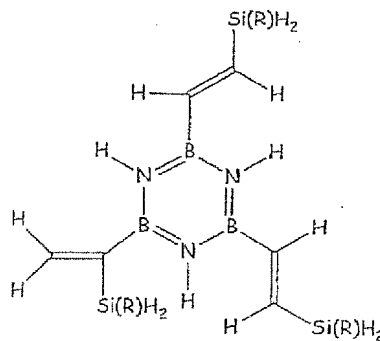
$^{29}\text{Si-NMR}$: -36.3/ $^{11}\text{B-NMR}$: 31.7/ $^1\text{H-NMR}$: 3.7; 4.9; 6.6; 7.6/ $^{13}\text{C-NMR}$: 153.2; 139.5; 134.1; 131.9; 132.0; 128.5

In the case of B-tris((methyldihydrosilyl)vinyl)-borazine, the following analytical data were obtained:

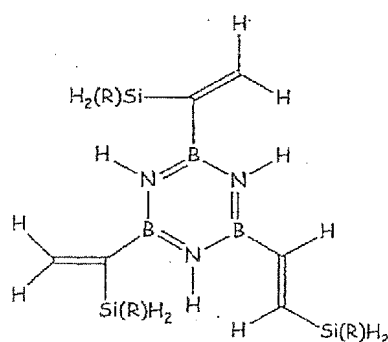
$^{29}\text{Si-NMR}$: -30.0/ $^{11}\text{B-NMR}$: 33/ $^1\text{H-NMR}$: 0.6; 3.5; 5.0; 6.8/ $^{13}\text{C-NMR}$: 151.4; 141.0; 4.6



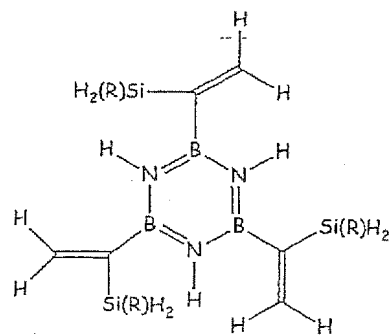
IVa



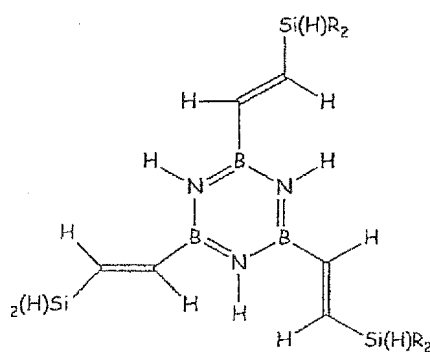
IVb



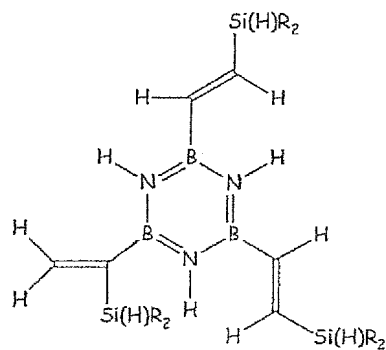
IVc



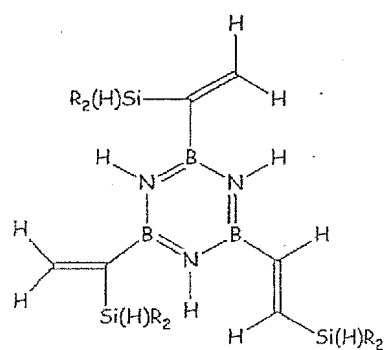
IVd



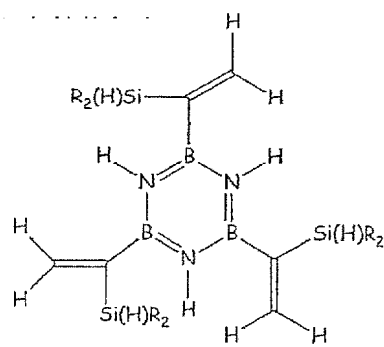
Va



Vb



Vc



Vd

The properties of the ceramic, in particular the electrical, thermal and mechanical properties, can be

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altered by choice of the R groups. In particular, it has been found that a higher proportion of carbon results in a higher conductivity of the ceramic, which can be explained by a higher proportion of double
5 bonds.

The precursor can be mixed with metal compounds in order to obtain a metal-doped ceramic. For example, this can be achieved by mixing the precursor with
10 organometallic compounds in a solvent, for example THF, acetonitrile, toluene, benzene or hexane, and subsequently pyrolyzing the product as above. Suitable metal compounds have been found to be, in particular: $\text{Fe}(\text{CO})_5$, $\text{Fe}_2(\text{CO})_9$; ferrocene, bis(1,5-cyclooctadiene)-
15 nickel(0), $\text{LiHB}(\text{CH}_2\text{CH}_3)_3$, $(i\text{But})_2\text{AlH}$. The metal atoms or clusters can be distributed very homogeneously on a nano scale. Up to 1500°C , an amorphous distribution and a metal content up to about 3% are obtained. The thermal decomposition can be accelerated by means of UV
20 radiation.

Figure 1 shows a micrograph of an iron-doped ceramic, in which the iron is visible as black areas which have a size up to only a few nanometers.

25

A metal-doped ceramic has an increased electrical conductivity. It can, for example, be heated inductively without contacts by means of an electric field. Such a ceramic can be used, for example, for producing a
30 medical implant. Such a doped ceramic can also be used as a magnetic memory. The magnetic information can, for example, be cleared thermally or by means of an AC field.

35 The process of the invention is also suitable for producing ceramic particles which are coated with

carbon nanotubes, as shown in figure 2.

As catalyst for the formation of the nanotubes, use was made of Ni which had been mixed in the form of a suitable soluble compound into the liquid precursor. The nanotubes are formed in situ on the entire surface of the ceramic during the pyrolysis. Very small parts having a high density of nanotubes can be obtained. The nanotubes are suitable, for example, as catalyst supports. The high thermal and chemical stability of the ceramic substrate is advantageous here.

B-Tris(hydrosilylvinyl)borazine is liquid at room temperature after the addition of even a small amount of solvent and can be applied as such by means of a brush or by spraying. The spreading properties can be adjusted by means of a suitable solvent. This is particularly important for the application of thin layers. An appropriate thixotropy can likewise be set here. In this way, different layer thicknesses can be ensured precisely. For example, the insides of pipes can be coated with B-tris(hydrosilylvinyl)borazine or solutions thereof.

Pyrolysis of B-tris(hydrosilylvinyl)borazine converts it into a ceramic material in a surprisingly high yield. The ceramic yield was 94% in the abovementioned examples. The pyrolysis is preferably carried out using a prepyrolysis at a temperature below 1000°C and a pyrolysis at a temperature of from > 1000°C to about 2000°C. The ceramic material can also be produced by pyrolysis of the isomeric compounds or from a mixture of isomers.

An important advantage of this method of production is that no crosslinking and polymer formation is

necessary. The B-tris(hydrosilylvinyl)borazine is converted directly into ceramic by pyrolysis. During the pyrolysis, essentially only hydrogen is released as decomposition product. This gives a ceramic which is
5 essentially pore-free and very dense. The shrinkage during pyrolysis is very low. A surprising additional aspect is the high stability of the ceramic, which can be explained by better crosslinking due to the many double bonds. The comparatively large number of double
10 bonds and the substantial absence of oxygen gives a conductive ceramic. This leads to the following preferred uses of the ceramic produced by this process:

Owing to the high thermal stability and electrical
15 conductivity, the ceramic is particularly useful for the production of heating elements and in particular contact-free heating elements. The conductivity of the ceramic of the invention can be seen from the measured curve in figure 3.

20

A further important advantage is the comparatively high air stability of the ceramic. This air stability is also present at high temperatures.

25 A further preferred use is the production of ceramic coatings. Owing to the comparatively high electrical conductivity, such coatings are antistatic. In addition, they are thermally and chemically stable. In particular, it is possible to produce coatings on the
30 inside of pipes, for example for the transport of liquids. Coating is effected by means of B-tris(hydrosilylvinyl)borazine, for example by painting or spraying. It is likewise possible to apply solutions of this compound. The ceramic can also be added, for
35 example as powder, to known coating compositions, for example to increase the conductivity. The ceramic is

particularly suitable for the production of enamels, since the ceramic retains properties, in particular the conductivity, even at relatively high temperatures. After application, pyrolysis is carried out.

5

The properties of the ceramic can be altered by the molecules of the precursor being crosslinked, preferably one-dimensionally or two-dimensionally, prior to pyrolysis. In particular, the borazine
10 molecules can be crosslinked in a chain-like manner by crystallization, with mixed crystals also being conceivable. Such crosslinking prior to pyrolysis results in the ceramic having a higher flexibility. This flexibility can be influenced by the degree and
15 type of crosslinking prior to pyrolysis and can thus be matched to the desired properties.

Further uses and applications of the ceramic of the invention are conceivable. In particular, various
20 semiconductor components can be produced using the ceramic.

Claims

1. A process for producing a B/N/C/Si ceramic from a borazine precursor, characterized in that the
5 borazine precursor is B-tris(hydrosilylvinyl)-borazine and this is converted into ceramic by pyrolysis.
2. The process as claimed in claim 1, characterized
10 in that the B-tris(hydrosilylvinyl)borazine is prepared by hydrogenation of B-tris(trichlorosilylvinyl)borazine.
3. The process as claimed in claim 2, characterized
15 in that the B-tris(trichlorosilylvinyl)borazine is prepared from B-triethynylborazine by hydrosilylation.
4. The process as claimed in claim 1, characterized
20 in that the B-tris(hydrosilylvinyl)borazine is pyrolyzed.
5. The process as claimed in any of claims 1 to 4,
25 characterized in that the B-tris(hydrosilylvinyl)-borazine is applied in liquid form and is subsequently pyrolyzed.
6. The process as claimed in claim 5, characterized
30 in that B-tris(hydrosilylvinyl)borazine is dissolved in a solvent and is made thixotropic.
7. The process as claimed in claim 5 or 6, characterized
35 in that B-tris(hydrosilylvinyl)borazine or a solution thereof is applied by painting or spraying and is subsequently pyrolyzed.

8. The process as claimed in any of claims 1 to 7, characterized in that the B-tris(hydrosilylvinyl)-borazine is, after a prepyrolysis, converted into a high-temperature ceramic at a higher temperature in the range from 1000°C to 2000°C, in particular 1100-1300°C.
9. The process as claimed in any of claims 1 to 8, characterized in that the precursor is doped with a metal or a metal compound to produce a doped ceramic.
10. The process as claimed in any of claims 1 to 9, characterized in that the molecules of the borazine precursor are one-dimensionally or two-dimensionally crosslinked prior to the pyrolysis.
11. The process as claimed in claim 1, characterized in that the precursor is B-tris((phenyldihydrosilyl)vinyl)borazine, B-tris((methyldihydrosilyl)vinyl)borazine or an amine.
12. A ceramic produced as claimed in claim 1, characterized in that it is substantially pore-free.
13. The ceramic as claimed in claim 12, characterized in that it is a substantially oxygen-free high-temperature ceramic.
14. The ceramic as claimed in claim 12, characterized in that it is a semiconductor.
15. The ceramic as claimed in claim 12, characterized in that it has been doped with metal.
16. The use of the ceramic produced as claimed in

claim 1 for producing a heating element.

17. The use of the ceramic produced as claimed in claim 1 for producing a coating.

5

18. The use as claimed in claim 15, characterized in that the coating is antistatic.

10 19. The use as claimed in claim 15, characterized in that the coating is an interior coating, in particular of a pipe.

20. The use of the ceramic produced as claimed in claim 1 for producing a semiconductor.

15

21. The use of the ceramic produced as claimed in claim 1 as a medical implant.

20 22. The use as claimed in claim 21, characterized in that the ceramic has been doped with metal.

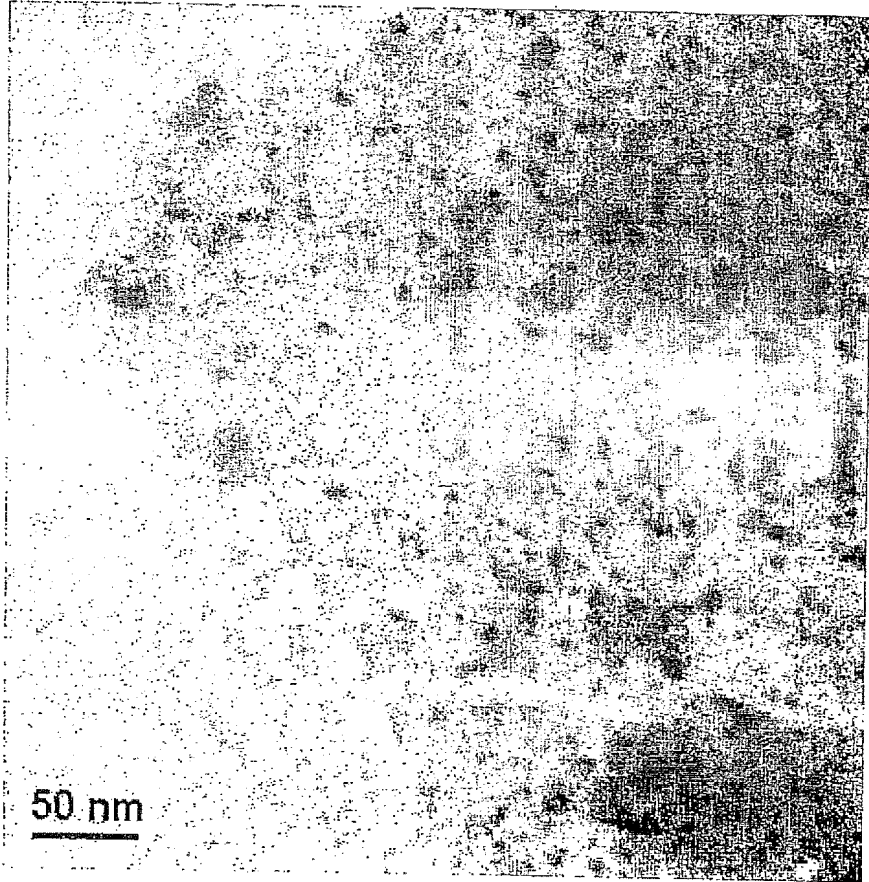


Fig. 1

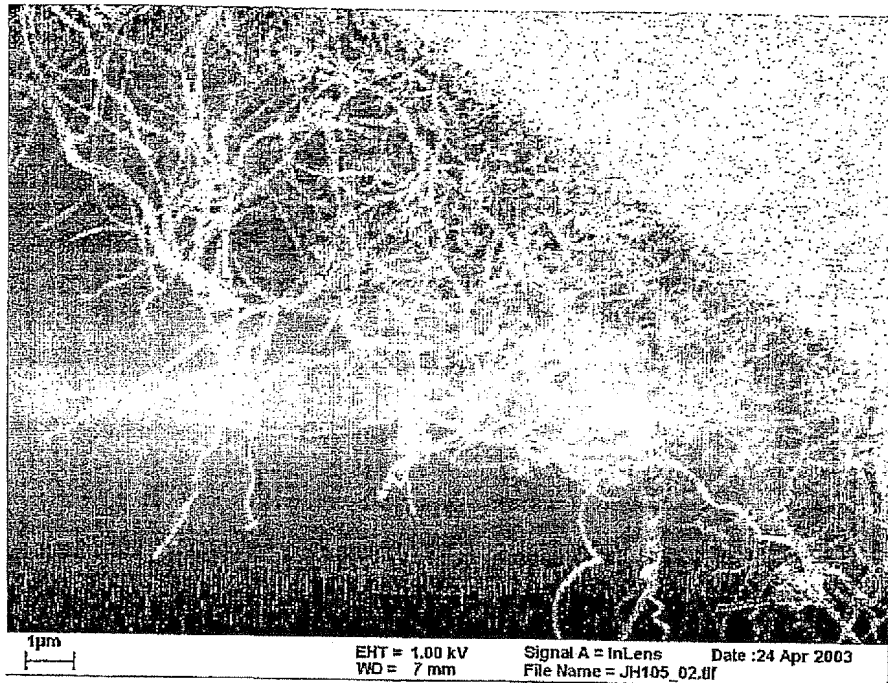


Fig. 2

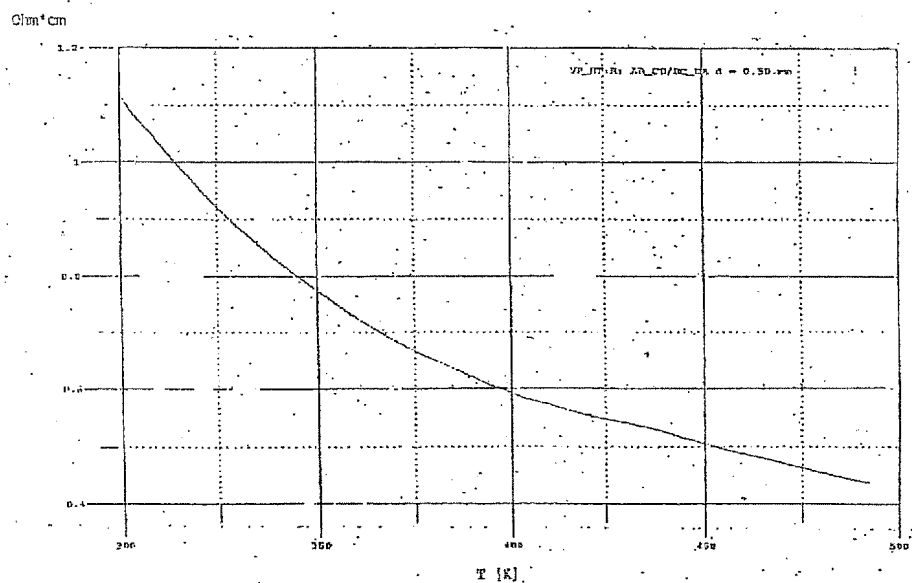


Fig. 3